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Photochemistry and Spectroscopy Laboratory

Department of Chemistry

Progress Report #1

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## 1. General Information

Although the grant award gives March 24, 1967 as the starting date for this investigation, active research was not commenced until about July 1, 1967. The reason for the delay is that we were not able to obtain the qualified research assistant and postdoctoral research associate at an earlier time.

We are happy to report that Miss Carolyn Kendrow, B.S. and M.S. University of Massachusetts, has joined us on July 1, 1967 as the research assistant under this grant. Miss Kendrow has extensive teaching experience at the University of Massachusetts and at Regis College. She has an excellent graduate school record, and has already passed the Ph.D. qualifying examinations here.

A large number of applications were processed for the postdoctoral associateship. We are fortunate to have been able to hire Dr. Philip Russell, who has impressive qualifications for this project. Dr. Russell joined us on October 15, 1967. His doctoral work was carried out with Professor A.C. Albrecht at Cornell University, and dealt with phosphorescence and fluorescence studies of benzene. Dr. Russell also spent several years doing postdoctoral research in spectroscopy with Professor D.S. McClure at the University of Chicago.

To date we have been primarily concerned with a literature survey of metal compounds. On the basis of this survey, two systems have been chosen for detailed study. The following section summarizes these activities and outlines the planned experimental work.

## 2. Research Activities

### A. Literature Survey

In accordance with the approach outlined in the proposal, we have surveyed the literature on metallic compounds for systems potentially capable of lasing. Several considerations shaped the direction of the search. These were:

- (1) From a practical point of view, which is dictated by our current detection capability, the transition corresponding to the laser action should be in the visible or the near infrared portion of the spectrum.
- (2) Sharp emission in this spectral range is invariably characteristic of either atomic states or of states of small symmetric molecules in the gaseous state.
- (3) Laser action from a reversible process is more desirable than one which involves the production of stable products via complex paths.

Three classes of compounds emerged as potential sources of investigation.

Metal Carbonyls - There is experimental evidence that the primary photochemical step in the photolysis of  $M(CO)_n$  compounds is decomposition to  $M(CO)_{n-1}$  and CO.<sup>1</sup> Further, emission from vibrationally excited CO has been reported.<sup>2</sup> Higher vibrational levels of CO have been populated by energy transfer from excited mercury atoms,<sup>3</sup> and laser action involving vibrational transitions has been reported.<sup>4</sup> The general problem of vibrational-rotational population inversion has been examined in some detail by Polanyi.<sup>5</sup>

At first sight, then, the carbonyls would appear to be good candidates for a CO laser. Several considerations, however, indicate otherwise. There is no detailed knowledge of the fate of the  $M(CO)_{n-1}$  fragment, and recombination of this fragment with a ground state CO molecule is not likely to be rapid in relation to the CO transitions. Further, it appears that if two fragments result from the photodissociation of a polyatomic molecule, the more complete fragment is generally more likely to retain the excess energy. From this point of view one would not expect the photodecomposition of carbonyls to efficiently populate higher vibrational levels in the eliminated CO molecule.

Our ardor to investigate this class of compounds was further dampened by repeated reports of their extraordinary toxicity.

Metal Chelates - Chelates of many metals are known to emit strongly in solution; in fact, these systems are used as sensitive analytical tests for the metal ion.<sup>6</sup> Laser action from chelates in solution is now well-substantiated. However, as expected, the emission is rather broad and the gains are generally low.

In the chelates of transition metals, photolysis can entrap excitation in d-d or f-f forbidden transitions. The d-d energy gap will be a function of the ligand field and might be expected to vary with chelate geometry. This has recently been shown to be the case for the transition metal halide spectra.<sup>7</sup>

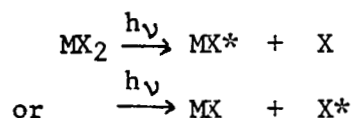
No fluorescence data have been reported for metal chelates in the gaseous state. Although thermal stability and volatility are indicated for the metal derivatives of several ligands, vapor pressure information

is lacking. The gaseous state offers many advantages over condensed phases for laser activity. In particular, lattice-coupled radiationless quenching mechanisms are eliminated. Certain chelates which are reported not to show emission in solution<sup>6</sup> may well do so as a vapor, and a gas phase study of these compounds is considered to be potentially fruitful.

Metal Halides - These are the most promising of the systems surveyed.

(1) Halides of the Type MX<sub>2</sub>

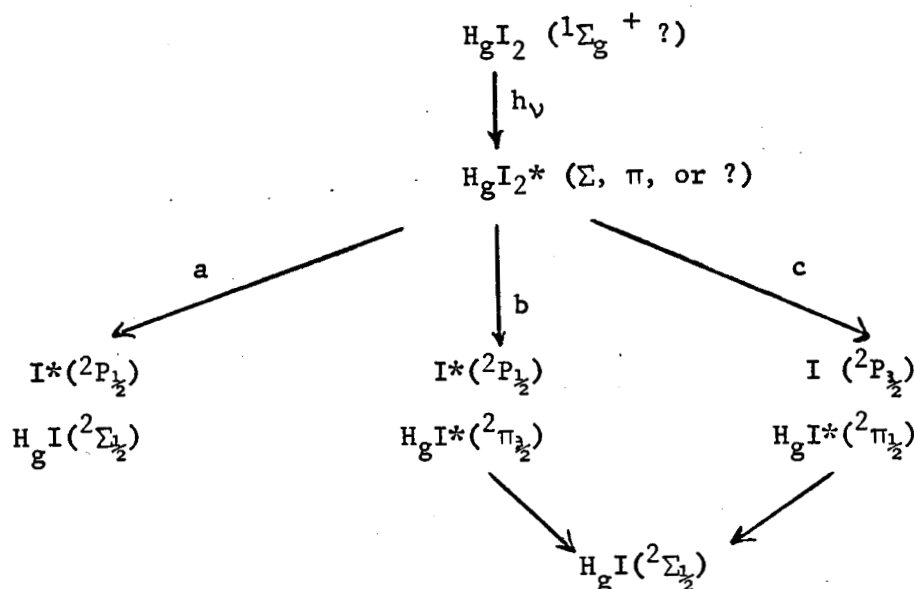
Terenin and his group investigated the photochemistry of several of these compounds in the late 1920's and early 1930's and reported that either



can occur, with high energy radiation favoring the former process.<sup>8</sup> Here X\* is presumed to be the  $^2\text{P}_{1/2}$  state of the halogen atom. In the case of iodine, the  $^2\text{P}_{1/2} \leftarrow ^2\text{P}_{3/2}$  transition has a ca. 7000 cm<sup>-1</sup> spacing and a 0.1 sec lifetime. The metal halide photodissociation system has the advantage over a conventional iodine laser in that it is likely to be reversible.

Reliable spectroscopic information is available only for mercury-iodine compounds. HgI<sub>2</sub> is linear to  $\pm 20^\circ$  so that its ground state is most likely  $^1\Sigma_g^+$  (or  $^1\text{A}_1$  if bent). The only excited states of HgI for which emission has been characterized are  $^2\pi_{1/2}$  (D) and  $^2\pi_{3/2}$  (C).<sup>9</sup> These states lie approximately 30,000 cm<sup>-1</sup> above the ground state and about 3500 cm<sup>-1</sup> apart. There are also uncharacterized A and B states. The ground state is  $^2\Sigma_{1/2}$  (X).

Transitions  $D \rightarrow X$  and  $C \rightarrow X$  are of the Hund's Case a type, and are allowed under the appropriate selection rules. Application of both the selection rules and angular momentum conservation considerations leads to the following schemes.



Path a is allowed only through spin-orbit coupling which, in the case of atoms as heavy as those involved here, would be expected to be strong. Paths b and c are strongly allowed. One sees three possibilities of population inversion and laser action:

Inversion of the population of the  $2P_{1/2}$  and  $2P_{3/2}$  states of iodine, which is a strong possibility; inversion of the population of the  $2\pi_{1/2}$  and  $2\pi_{3/2}$  states of excited  $\text{HgI}$ , which is less likely; and finally, recombination reactions producing triplet states of  $\text{HgI}_2$  which, though probable, are unlikely to lead to inversion due to the strong spin-orbit coupling. Inasmuch as the rates of competitive processes ultimately determine population inversion, only experiment can show the laser feasibility of this system.

Iodides are the most desirable halides for initial study in that the lasing would most probably occur near  $1.3\mu$ , and will be easy to detect and characterize. Iodides are also more volatile than the other halides, which will permit operation at lower temperatures. Of the halides considered here,  $HgI$  is the only diatomic fragment whose upper states have been unambiguously characterized by rotational analysis. Mercuric iodide, the most favored candidate, suffers the disadvantage of a lower iodide,  $Hg_2I_2$  which may limit reversibility. Again, only experimentation will reveal possible limitations from this source.

(2) Halides of the Type  $MX_n$  ( $n > 2$ )

Terenin reported that when  $SnI_4$  or  $BiI_3$  are photolyzed, excited  $I_2$  is a primary photoproduct.<sup>10</sup> There are sufficient questions that can be raised concerning the experimental procedures and the interpretation of their results as to cast doubts on this conclusion. With a lifetime of less than one microsecond for excited  $I_2$ , population inversion with respect to this state will be difficult to achieve. The dissociation of  $I_2^*$  leads to equal populations of the  $^2P_{1/2}$  and  $^2P_{3/2}$  atomic states. The  $MX_n$  halides are thus only marginal candidates for potential laser action. It is further our feeling that the original photochemical work on these compounds needs to be repeated.

(3) Halides of the Type  $MX$

In all cases, the volatilities of these compounds are inconveniently low. Photodissociation almost invariably leads to excited metal atoms. However, the photochemical reaction  $MX \xrightarrow{h\nu} M + X^*$  has been reported.<sup>11</sup>

## B. Experimental Program

On the basis of the literature survey, we have decided to investigate a number of the metal halides of the type  $\text{MX}_2$  and some metal chelates in the vapor phase.

The metal halides selected are those of mercury, zinc, cadmium, lead and calcium. These compounds have volatilities such that experiments can be performed at reasonable temperatures. The first compound studied is mercuric iodide, and this will be followed by other iodides. There are abundant thermodynamic data on these compounds which permit calculation of the composition of the vapor in equilibrium with the solid at the temperatures of interest. A computer program is being written to provide this information. The sequence of planned experimental work is as follows.

- (1) Measurement of the absorption spectra of gaseous  $\text{MX}_2$  and of matrix-isolated  $\text{MX}_2$ .
- (2) Measurement of the emission spectra to wavelengths of several microns. An attempt will be made to estimate the lifetime of the emission.
- (3) Flash photolysis experiments to determine the kinetic behavior and spectral characteristics of the photodissociation fragments.
- (4) Cavity experiments for laser activity.

The chelates to be studied are those involving the transition metals, rare earths, copper and thallium with  $\beta$ -diketones and 8-hydroxyquinoline as ligands. A number of the  $\beta$ -diketone chelates have already been procured and will be purified. First, the thermal stability and vapor pressures will be determined. The vapor state



emission and absorption spectra will be measured and compared with solution results. Laser action experiments will be performed if this spectral survey furnishes promising compounds.

The construction of apparatus for these experiments is underway. The modification of the 500-mm Jarrell-Ash spectrometer for long-path absorption and emission measurements is almost completed. We have also designed and are now building a  $\frac{1}{2}$ -meter long quartz absorption cell with precise temperature regulation to 700°C. Cells for high temperature emission and flash experiments are still in the design stages.

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